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(54) SELECTIVE CONVERSION OF HIGH-MOLECULAR WEIGHT FULLERENE TO C60

(57)Abstract:

PURPOSE: To provide a process for converting a less important high-molecular weight fullerene having carbon atoms of  $\geq 70$  (C70+) into more useful fullerene C60 in high selectivity and efficiency.

CONSTITUTION: High molecular weight fullerene having carbon atoms of  $\geq 70$  and a closed shell structure is hydrogenated under a hydrogen pressure of 30-180 kg/cm<sup>2</sup>G at 80-240°C in the presence of a hydrogenation catalyst and the obtained hydrogenation product is dehydrogenated to effect selective conversion of the high-molecular weight fullerene into C60 fullerene.

[Claim(s)]

[Claim 1]The fullerene of the with a carbon numbers of 70 or more amount of polymers which have closed shell structure under existence of a hydrogenation catalyst under hydrogen pressure 30-180kg/cm<sup>2</sup>G and conditions with a temperature of 80-240 \*\*, The alternative converting method to C<sub>60</sub> of the amount fullerene of polymers carrying out dehydration of the hydride which hydrogenated and was produced by ranking second.

[Detailed Description of the Invention]

[0001]

[Industrial Application]When this invention is said in more detail about the alternative

converting method to  $C_{60}$  of the amount fullerene of polymers, it relates to the method of converting the fullerene of the with a carbon numbers of 70 or more amount of polymers into more useful fullerene  $C_{60}$  with sufficient selectivity.

[0002] Fullerene  $C_{60}$  is expected from various uses including the derivative.

For example, it is useful as those synthetic powder as exotic materials in various kinds of fields, such as electrical and electric equipment, electronic industry materials, etc., such as an electrical conducting material and a raw material of a super-conductor, and new materials.

[0003]

[Description of the Prior Art] These days, the molecule-like carbon substance new type called the carbon cluster (spherical giant molecule) of the closed shell structural form of the carbon numbers 60 and 70 and 84 grades is compounded, and attracts attention. The carbon cluster which has this special structure is also called fullerene, is called fullerene  $C_{60}$ , the  $C_{70}$ , the  $C_{84}$ , etc. by the carbon number which constitutes that molecular skeleton, or is only called  $C_{60}$ ,  $C_{70}$ ,  $C_{84}$ , etc. Such fullerene is new carbon materials.

Since it is expected that unique physical properties will be shown also from having special molecular structure, research on the character and application development is advanced briskly.

[0004] It is the most fundamental fullerene with sufficient symmetry by the football type real ball-like unsaturation molecule from which  $C_{60}$  is constituted by six membered-rings and the five-membered ring also in the fullerene of the carbon number of these various kinds.

It is comparatively stable, and since it is easy to manufacture, attention is attracted especially in various kinds of areas of investigation and applicable fields, and expectation is the greatest also in respect of the use as a material with versatility new including the derivative.

[0005] thus, fullerene  $C_{60}$  forms the fields for 1 Otoshi including the derivative, and is especially useful as a raw material of a superconductor, etc. -- etc. -- the usefulness is becoming clear.

In various kinds of fields of the invention including the electrical and electric equipment and the electronic field, the expectation as an exotic material and new materials is becoming actual.

[0006]However, the fullerene of the with a carbon numbers [ , such as  $C_{70}$ , ] of 70 or more amount of polymers isolates, and although it is the stage currently studied, it is becoming clear that character, such as superconductivity which is looked at by fullerene  $C_{60}$ , is not shown.

[0007]That is, as industrial importance of these fullerene, the  $C_{60}$  is much larger than other fullerene, such as  $C_{70}$ , and establishment of the art for obtaining fullerene  $C_{60}$  with more sufficient selectivity is desired strongly.

[0008]By the way, such fullerene is compounded by evaporating graphite by arc discharge (resistance heating method), or making it evaporate by a laser beam generally. In any case, it is obtained as soot containing the mixture of the fullerene of various kinds of carbon numbers.

There is little fullerene contained in this soot as about at most 10 % of the weight in all, among those fullerene, about 80 to 90% is fullerene  $C_{60}$ , and about 10 to 15% is  $C_{70}$ , and the other amount fullerene of polymers is also usually contained at a rate of several percent. Thus, although there is most fullerene  $C_{60}$  in the fullerene obtained, the byproduction of the fullerene ( $C_{70+}$ ) of the amount of polymers more than  $C_{70}$  is carried out at a remarkable rate. Separate recovery of the fullerene obtained as a mixture in soot is carried out by solvent extraction, chromatography separation, etc. as presentation fullerene, refining fullerene, isolation fullerene, etc.

[0009]Here, for the thing with large demand made the most important on industry and research to be fullerene  $C_{60}$  which shows superconductivity etc., and to raise the productive efficiency further, as described above is needed. On the other hand, from those, such as  $C_{70}$ , since the important position is not occupied so industrially, for the moment, the amount fullerene of polymers ( $C_{70+}$ ) seldom expects the remarkable increase in the demand, even if demand will see few especially also in the actual condition in the future. Therefore, unless the art of manufacturing fullerene  $C_{60}$  very selectively is developed, it is expected that the quantity of production of fullerene other than fullerene  $C_{60}$  becomes increasingly superfluous, so that the production quantity of fullerene increases.

[0010]Thus, in the production technology of the conventional fullerene, the badness of the balance of the quantity of production (comparatively) that shortage of fullerene  $C_{60}$  and the amount fullerene of polymers ( $C_{70+}$ ) are superfluous based on the remarkable difference in demand or usefulness had become a big problem.

[0011]

[Problem(s) to be Solved by the Invention]This invention is made in view of the

above-mentioned situation. The purpose of this invention is to provide the method of selectivity being good for more useful fullerene  $C_{60}$ , and converting efficiently the fullerene ( $C_{70+}$ ) of the with a carbon numbers [ with little importance ] of 70 or more amount of polymers.

[0012]

[Means for Solving the Problem]When the fullerene of the amount of polymers with larger carbon numbers, such as fullerene  $C_{70}$ , than 60 could be converted into fullerene  $C_{60}$  with sufficient selectivity, this invention persons thought that it was very effective also as a means by which the method solves said problem, and repeated research wholeheartedly about the method.

[0013]As a result, if the fullerene ( $C_{70+}$ ) of the with a carbon numbers [ , such as fullerene  $C_{70}$ , ] of 70 or more amount of polymers is hydrogenated by a specific reaction condition (temperature and hydrogen pressure) using various kinds of hydrogenation catalysts, Hydrogenation of the these  $C_{70+}$  is not only carried out, but a very unique reaction called combination of an alternative reduction and hydrogenation to 60 of a carbon number occurred easily, and it found out a very important fact of converting into a hydride (hydrogenation thing) of fullerene  $C_{60}$  with yield often [ selectivity ] and sufficient. Hydrogenation products (namely, the hydrogenation fullerene containing hydrogenation fullerene  $C_{60}$  of raw material fullerene  $C_{70+}$  origin) of  $C_{70+}$  obtained in this way, It turned out that dehydration can be easily carried out on condition of various kinds after separation suitably, and hydrogenation fullerene  $C_{60}$  can be easily converted into fullerene  $C_{60}$  according to this dehydration also with a mixture. With namely, combination of these unique hydrogenation reactions and the usual dehydrogenation. The new art in which the fullerene of the with a carbon numbers [ , such as  $C_{70}$  with little importance, ] of 70 or more amount of polymers could be converted into more important fullerene  $C_{60}$  often [ selectivity ] and efficiently was able to be developed. In this new technology, other hydrogenation fullerene other than hydrogenation fullerene  $C_{60}$  generated by hydrogenation of raw material fullerene  $C_{70+}$  can be converted into fullerene corresponding according to that dehydration, Again, since it also used effectively as raw material fullerene  $C_{70+}$  etc., also in this point, it was able to check that it was an efficient process.

[0014]This invention persons came to complete this invention based on these knowledge.

[0015]Namely, this invention the fullerene of the with a carbon numbers of 70 or more amount of polymers which have closed shell structure under existence of a hydrogenation catalyst under hydrogen pressure 30-180kg/cm<sup>2</sup>G and conditions with a temperature of 80-240 \*\*, The alternative converting method to  $C_{60}$  of the amount

fullerene of polymers carrying out dehydration of the hydride which hydrogenated and was produced by ranking second is provided.

[0016] In a method of this invention, the fullerene (this may be hereafter called raw material fullerene  $C_{70+}$ .) of the with a carbon numbers of 70 or more amount of polymers which have closed shell structure is used at least as a raw material or a raw material component of said hydrogenation process. It is usable also in what this raw material fullerene  $C_{70+}$  has the closed shell structure which consists of a carbon atom peculiar to fullerene, and will be depended on what kind of kind and manufacturing method if a carbon number is 70 or more. As this raw material fullerene  $C_{70+}$ , Various kinds of fullerene shown by fullerene  $C_n$  (however,  $n$  expresses 70 or more integers.), a thing which are fullerene and is specifically shown by  $C_{70}$ ,  $C_{76}$ ,  $C_{78}$ ,  $C_{80}$ ,  $C_{82}$ ,  $C_{84}$ , etc., for example, etc. can be mentioned. These may be used by an one-sort independent and can also use two or more sorts as a mixture etc. With a carbon numbers [ these ] of 70 or more fullerene. Are usable also as a thing of various purity which contains other ingredients in the range which does not check the purpose of this invention, or the degree of refining, For example, it can also be used as the crude fullerene containing both other fullerene, such as other fullerene (for example, fullerene  $C_{60}$  etc.), mixed fullerene of a mixture, and fullerene  $C_{60}$ , a state thing which has still lower purity containing both soot. On said hydrogenation conditions in a method of this invention, if it converts into a hydride of fullerene  $C_{60}$ , It is usable as raw material fullerene  $C_{70+}$  or its ingredient also in derivatives (for example, metallofullerene  $C_{70+}$ , fullerene  $C_{70+}$  already hydrogenated, alkylation fullerene  $C_{70+}$ , etc.) of various kinds of with a carbon numbers of 70 or more fullerene.

[0017] In a method of this invention, although it hydrogenates using hydrogen gas under existence of a suitable hydrogenation catalyst, using said raw material fullerene  $C_{70+}$  as a raw material or a raw material component, It is important for this hydrogenation reaction to carry out under specific conditions of a range whose hydrogen pressure is the range of  $30 \sim 180 \text{ kg/cm}^2\text{G}$  and whose temperature is  $80 \sim 240^\circ\text{C}$ . By performing said hydrogenation on this condition, raw material fullerene  $C_{70+}$  can be converted into a hydride of fullerene  $C_{60}$  often [ selectivity ] and efficiently at least. Although all of these raw material fullerene  $C_{70+}$  can also be converted into hydrogenation fullerene  $C_{60}$  depending on conditions, hydrogenation fullerene  $C_{70+}$  which is a hydrogenation thing of raw material fullerene  $C_{70+}$  is also usually generated with hydrogenation fullerene  $C_{60}$ . When a raw material containing fullerene  $C_{60}$  is used, hydrogenation of the fullerene  $C_{60}$  in this raw material is carried out as it is, and it turns into hydrogenation fullerene  $C_{60}$ .

[0018] If hydrogen pressure in said hydrogenation reaction is less than 30 kg/cm<sup>2</sup>G, here, Even if hydrogenation reactions, such as raw material fullerene C<sub>70+</sub>, advance, an inversion rate and selectivity to hydrogenation fullerene C<sub>60</sub> of raw material fullerene C<sub>70+</sub> will become insufficient, On the other hand, about hydrogen pressure, the further improvement in an inversion rate to hydrogenation fullerene C<sub>60</sub> and selectivity cannot be found as a pressure exceeding 180 kg/cm<sup>2</sup>G, and it becomes disadvantageous in respect of an installation cost or energy cost on the contrary.

[0019] A reaction to hydrogenation fullerene C<sub>60</sub> of raw material fullerene C<sub>70+</sub> does not advance at sufficient speed that reaction temperature in said hydrogenation reaction is less than 80 \*\*, If the hydrogenation reaction itself becomes late and it makes reaction temperature higher than 240 \*\* on the other hand, decomposition of fullerene, such as raw material fullerene C<sub>70+</sub> and produced hydrogen-ized fullerene C<sub>60</sub>, and hydrogenation fullerene takes place easily, and neither of the cases can fully attain the purpose of this invention.

[0020] Since reaction time for performing this hydrogenation reaction suitably differs according to various conditions, such as a kind of hydrogenation catalyst, a using rate, a presentation of a raw material, reaction temperature, hydrogen pressure, etc. to be used, it cannot be defined uniformly, but it is usually enough in about 0.1 to 100 hours.

[0021] It is usable in various kinds of hydrogenation catalysts, such as a thing etc. of homogeneous catalysts and heterogeneous catalysts which restriction in particular does not have, and are used or proposed as a hydrogenation catalyst of publicly known hydrocarbon etc. as a hydrogenation catalyst used for said hydrogenation reaction, or such mixed stock. As such a hydrogenation catalyst, for example Cr, Fe, Co, nickel, If there is a catalyst of various gestalten which consist of various kinds of metal including transition metals, such as Mo, Ru, Rh, Pd, W, Re, Os, Ir, and Pt, and a typical thing of them is illustrated, For example, metal system catalysts, such as metallic colloid represented with Pt colloid, a Raney nickel catalyst, the Raney ruthenium, Raney cobalt, etc., Platinum black, palladium black, ruthenium black, rhodium black, A metallic-oxide system catalyst represented with rhenium black, chrome oxide, molybdenum oxide, etc., metallic-compounds system catalysts, such as a metallic sulfide system catalyst represented with a molybdenum sulfide and rhenium sulfide, and various kinds of metal complex system catalysts, -- further, Various kinds of supported type catalysts which support these metal or metallic compounds to various kinds of carriers. for example, Pd/carbon, Ru/carbon, nickel/diatomaceous earth, and Pd/silica. Various things, such as Pd/alumina, Pd/silica alumina, Ru/silica, Pt/silica, Pt/alumina, nickel/silica, Co/alumina, MORIBUDENA/alumina, chromia/alumina, Rh/silica,

Re/silica, can be mentioned. Pd/carbon, Ru/carbon, nickel/diatomaceous earth, etc. can be mentioned as what can be especially used conveniently also in these, for example. These hydrogenation catalysts may be used by an one-sort independent, and two or more sorts can be mixed, or can be composite-ized, and they can also use them together. [0022]As hydrogen gas used for said hydrogenation reaction, from the first, it is usable and various purity, such as a thing of various industrial use, or a thing of a grade can use a pure thing also as hydrogen gas content gas.

[0023]As for said hydrogenation reaction, although a non-solvent is also possible, it is preferred to usually carry out in a suitable solvent (or dispersing solvent) from points, such as to raise reactivity. As this solvent, various kinds of things are usable and For example, benzene, Alkanes, such as alicyclic hydrocarbon compounds, such as aromatic compounds, such as toluene, xylene, and mesitylene, cyclohexane, a methylcyclohexane, and dimethylcyclohexane, hexane, heptane, octane, and Deccan, can be illustrated. These may be used as an one-sort independent solvent, or can also use two or more sorts as a mixed solvent etc.

[0024]Also in these, since aromatic hydrocarbon system solvents, such as benzene, toluene, xylene, and mesitylene, have high solubility to various kinds of hydrogenation fullerene and also have solubility high enough also to various kinds of fullerene, they are preferred especially in respect of improvement in reactivity. However, since it usually converts into the cycloalkanes to which hydrogenation also of those aromatic compounds is carried out, and they correspond along with said hydrogenation reaction when these aromatic system compounds are used as a solvent or its ingredient, hydrogen will be consumed by that part excess in this case. Therefore, in respect of a solvent which does not consume hydrogen too much in this way, cycloalkanes and the alkanes are more advantageous.

[0025]On the other hand, although cycloalkanes and alkanes show solubility high enough to various kinds of hydrogenation fullerene, such as hydrogenation fullerene  $C_{60}$  which is a key objective compound of this hydrogenation reaction, Sufficient solubility is not shown to other carbon, such as fullerene, such as raw material fullerene  $C_{70+}$ , and graphite. Then, separation of the produced hydrogen-ized fullerene after a hydrogenation reaction can also be made easier using this.

[0026]By performing a hydrogenation reaction as mentioned above, raw material fullerene  $C_{70+}$  can be converted into hydrogenation fullerene  $C_{60}$  with selectivity and inversion rate high enough. As described above, depending on conditions, can also convert all of these raw material fullerene  $C_{70+}$  into hydrogenation fullerene  $C_{60}$ , but. Usually, hydrogenation fullerene  $C_{70+}$  which is a hydrogenation thing of raw material

fullerene  $C_{70+}$  is also generated with hydrogenation fullerene  $C_{60}$ .

[0027] Here, hydrogenation fullerene  $C_{60}$  generated from raw material fullerene  $C_{70+}$  by said hydrogenation is usually obtained as a mixture of various kinds of hydrogenation fullerene  $C_{60}$  in which H/C ratios differ, although a carbon number is 60. Specifically, it is obtained as a mixture of a compound of various kinds of H/C ratios expressed with general formula  $C_{60}H_m$  ( $m$  usually shows about 30 to 44 integer.), for example. As an example of each compound of this hydrogenation fullerene  $C_{60}$  obtained, For example,  $C_{60}H_{30}$ ,  $C_{60}H_{32}$ ,  $C_{60}H_{34}$ ,  $C_{60}H_{36}$ ,  $C_{60}H_{38}$ ,  $C_{60}H_{40}$ ,  $C_{60}H_{42}$ ,  $C_{60}H_{44}$ , etc. can be illustrated. A thing of these compounds which you control those rates using this, or is made to generate selectively hydrogenation fullerene  $C_{60}$  of a specific H/C ratio since it changes with said hydrogenation conditions comparatively (composition ratio) is also possible. Therefore, a method of this invention can be used also as a method of manufacturing hydrogenation fullerene  $C_{60}$  of various kinds of H/C ratios like the above from various kinds of raw material fullerene  $C_{70+}$ . However, since dehydration of the hydrogenation fullerene  $C_{60}$  is carried out and it is considered as fullerene  $C_{60}$  for the main purpose of this invention, if a mixture of hydrogenation fullerene  $C_{60}$  which has distribution in a H/C ratio is obtained by said hydrogenation reaction, it will come out enough, and will be and hydrogenation fullerene  $C_{60}$  of a specific H/C ratio will not be made to not necessarily generate selectively -- also coming out -- it is good. Conditions to which selection of a hydrogenation reaction becomes much more nearly free, and a direction of it becomes larger about selectivity and an inversion rate to the whole hydrogenation fullerene  $C_{60}$  can be chosen easily.

[0028] On the other hand, by said hydrogenation reaction, a hydrogenation thing of raw material fullerene  $C_{70+}$  is generated, and, generally this hydrogenation thing is also usually generated as a mixture of various kinds of H/C ratios. For example, as hydrogenation fullerene  $C_{70}$  to generate, usually, a compound of various kinds of H/C ratios expressed with general formula  $C_{70}H_k$  ( $k$  usually shows about 30 to 46 integer.) being mentioned, and specifically,  $C_{70}H_{30}$ ,  $C_{70}H_{32}$ ,  $C_{70}H_{34}$ ,  $C_{70}H_{36}$ ,  $C_{70}H_{38}$ ,  $C_{70}H_{40}$ ,  $C_{70}H_{42}$ ,  $C_{70}H_{44}$ ,  $C_{70}H_{46}$ , etc. can be illustrated. These rates are also good not to control the presentation by adjustment of hydrogenation conditions etc., in particular in order to be the main purpose of this invention although it is controllable. Hydrogenation fullerene other than hydrogenation fullerene  $C_{60}$  obtained in this way. After being able to dissociate suitably, being able to collect, also being able to use for the various purposes, carrying out dehydration and returning to fullerene, such as fullerene  $C_{70+}$ , before performing dehydration, it can also use again as a raw material of said hydrogenation reaction in a method of this invention, or its ingredient.



[0029]By said hydrogenation reaction, raw material fullerene  $C_{70+}$  can be converted into desired hydrogenation fullerene  $C_{60}$  with a high inversion rate with sufficient selectivity as mentioned above, Hydrogenation products containing many hydrogenation fullerene  $C_{60}$  of various kinds of H/C ratios like the above can be obtained efficiently.

[0030]In a method of this invention, hydrogenation fullerene  $C_{60}$  obtained at least is converted into fullerene  $C_{60}$  by carrying out dehydration of the hydride which is the output acquired by said hydrogenation. Since hydrogenation fullerene  $C_{60}$  is converted into fullerene  $C_{60}$  of the same carbon number by this dehydration, hydrogenation fullerene  $C_{60}$  obtained by said hydrogenation reaction can also be made to convert into fullerene  $C_{60}$  quantitatively made into the purpose. It can be made to convert into fullerene  $C_{60}$  which selectivity is good and targets raw material fullerene  $C_{70+}$  used as a result with high yield by this.

[0031]This dehydrogenation is possible also for carrying out directly to output of said hydrogenation reaction, and good in backward [ which performed separating operation to this output suitably ]. Namely, if needed, after carrying out separation removal of a solvent, a catalyst, the impurity, etc., may carry out, and separate recovery of the hydrogenation fullerene  $C_{60}$  is carried out, On the other hand, may perform dehydration and, Or separate recovery is carried out as a mixture of hydrogenation fullerene  $C_{60}$  and other hydrogenation fullerene (hydrogenation fullerene  $C_{70+}$  etc. which is a hydrogenation thing of raw material fullerene  $C_{70+}$ ), Dehydration may be given to this mixed water matter-ized fullerene, and various modes can be chosen according to a case. When separating parts for an insoluble solid, such as a solid catalyst and an insoluble impurity, filtration, centrifugal separation, etc. can perform this easily, for example, and when performing separation removal of a solvent, this can be easily performed by the usual techniques, such as distillation (evaporation). In removing this, using a complex compound catalyst for example as a hydrogenation catalyst, after changing into insoluble solid residue by making this decompose well, a method of removing by filtration, centrifugal separation, etc. is also adopted suitably.

[0032]Anyway, dehydration is given to a hydrogenated mixture which contains at least said hydrogenation fullerene  $C_{60}$  or this which was generated from raw material fullerene  $C_{70+}$ .

[0033]As this dehydrogenation method, as long as it is the method of converting said hydrogenation fullerene  $C_{60}$  into fullerene  $C_{60}$  with selectivity sufficient enough at least, there is no restriction in particular and what kind of method may be used. For example, may carry out using various kinds of catalysts, such as a hydrogenation catalyst of the above-mentioned illustration, as a catalyst of this dehydrogenation, and. Or for example,

stoichiometrical things, such as inorganic system dehydration agents, such as organic system dehydration agents, such as 2,3-dichloro-5, 6-dicyanobenzoquinone (DDQ), a lead tetraacetate, mercury acetate (II), may be used, and it may use combining these.

[0034] Since the amount of these dehydrogenation catalysts or dehydration agent used changes with the kinds and changes with other conditions, such as the degree of hydrogenation of the hydrogenation fullerene which carry out dehydration, and reaction temperature, it cannot be defined uniformly, but it can determine the amount used easily by a preliminary experiment, calculation, etc.

[0035] This dehydrogenation can be performed in various kinds of solvents which do not have trouble in dehydrogenation, For example, it can carry out in that various kinds, such as a mixed solvent with cyclohexane and aromatic hydrocarbon, are still more independent, or mixed solvents, such as aromatic hydrocarbon, such as cyclohexane, such as a hydrogenation thing etc. of aromatic compounds used at the time of said hydrogenation reaction, benzene, toluene, and xylene. Also in these, aromatic hydrocarbon solvents, such as benzene, toluene, and xylene, or a mixed solvent which makes this the main ingredients is usually suitably used from points, such as efficiency of dehydrogenation. Since it excels also in solubility over the fullerene which such aromatic hydrocarbon raises contacting efficiency of a reaction, and have an advantage -- dehydration moreover is not carried out by dehydration agent -- and were generated according to dehydration, It becomes suitable also to separate recovery of fullerene, such as subsequent fullerene  $C_{60}$ .

[0036] reaction temperature of said dehydrogenation -- usually -- room temperature - it is appropriate preferably to consider [ 300 \*\* ] it as temperature of the range of 50-250 \*\*. In that case, a method of controlling reaction temperature, etc. are suitably adopted by REFURAKKUSU [ a solvent ]. Since advance of a reaction is slow or temperature of less than a room temperature generally takes cooling, it becomes disadvantageous in process and, on the other hand, is easy to produce trouble, like control of a reaction becomes difficult by a side reaction occurring at the same time at temperature over 300 \*\*.

[0037] Although it changes with other conditions, such as reaction temperature and a kind of dehydration agent, reaction time of this dehydrogenation is usually enough, if it is made into about 1 to 10 hours.

[0038] By the above dehydrogenation, hydrogenation fullerene  $C_{60}$  can be converted into fullerene  $C_{60}$  made into the purpose with high selectivity and an inversion rate at least. When hydrogenation fullerene other than hydrogenation fullerene  $C_{60}$  is contained in a raw material of this dehydrogenation, Since dehydration is carried out to the fullerene

to which these also correspond, inside it is the obtained fullerene, with a carbon numbers of 70 or more fullerene is also recyclable if needed as a raw material of said hydrogenation process at least. In order to raise process efficiency, it is desirable to make hydrogenation fullerene  $C_{60}$  convert into fullerene  $C_{60}$  quantitatively at least.

[0039] Thus, dehydration output containing fullerene  $C_{60}$  or fullerene  $C_{60}$ , and the other fullerene (for example, fullerene  $C_{70+}$ , such as fullerene  $C_{70}$ , etc.) can be acquired efficiently. These can remove unnecessary ingredients, such as an impurity originating in a catalyst or a dehydration agent, and a solvent, suitably if needed, and can collect them as mixed fullerene which use fullerene  $C_{60}$  of a high grade, and fullerene  $C_{60}$  as the main ingredients. Separate recovery of the fullerene of this request can be easily attained by various kinds of methods, such as a publicly known separation method.

[0040] For example, when generation fullerene, a dehydration agent, and its decomposition product are also dissolving using aromatic hydrocarbon of quantity sufficient as a solvent for dehydrogenation, the solution as it is, Or rinse a dehydration agent and its decomposition product, for example, and move to aqueous phase, or. When these are solids, after filtering and dissociating, soluble low fullerene is most deposited selectively by condensing a solution suitably. Although a method of fully distilling off low boiling point things, such as a way filtration etc. separate this, or a solvent, and separating fullerene as the evaporated residue, etc. are used suitably, it is not limited to these and is usable in various methods.

[0041] On the other hand, when a used solvent for dehydration has low solubility only to fullerene, such as fullerene  $C_{60}$ , for example From a reaction mixture to direct. Or after concentration, since removal by rinsing of a dehydration agent and its decomposition product, etc. is performed if needed, a way filtration etc. separate a sediment of desired fullerene etc. are adopted suitably.

[0042] The fullerene containing fullerene  $C_{60}$  separated in this way. If needed, a suitable solvent washes, extract, make it recrystallize, and also refining separating operation is performed, Further, fullerene  $C_{60}$  of a high grade and these can also be collected as mixed high fullerene of the degree of refining contained as the main ingredients, and fullerene other than fullerene  $C_{60}$  can isolate and use them effectively if needed. When fullerene  $C_{70+}$  remains in output acquired by said dehydration, By using this output as a raw material or a raw material component of said hydrogen reaction again, it can also convert effective in fullerene  $C_{60}$ , and yield of fullerene  $C_{60}$  can also be raised further further.

[0043] Of course, the fullerene  $C_{60}$  and fullerene  $C_{60}$  content mixing fullerene obtained as mentioned above can be collected in the state of a solution, and it can also use as a

product.

[0044]As explained in full detail above, by a method of this invention, selectivity is good and more useful fullerene  $C_{60}$  can be efficiently obtained from with a carbon numbers of 70 or more which are not industrially so important fullerene. It can carry out by the ability to also obtain hydrogenation fullerene  $C_{60}$  as an intermediate product in a method of this invention, and hydrogenation fullerene other than carbon number 60 as the by-product, etc. can be obtained.

[0045]Various kinds of products including these fullerene  $C_{60}$  can begin raw materials, such as a raw material of a superconductor, various kinds of electrical and electric equipment, electronic industry materials, and they can be used for them effective in a use wide range as synthetic powder of various derivatives, etc., for example.

[0046]

[Example]Hereafter, although the example of this invention and its comparative example explain this invention still more concretely, this invention is not limited to these examples.

[0047]Example 1  $C_{70}$ (98% of purity, impurity toluene 2%)200mg is dissolved in 500 ml of toluene, 5.0g added and a 5% ruthenium / carbon (50%wet) was made to react at 50 kg of hydrogen pressure/cm<sup>2</sup>G, and the temperature of 180 \*\* as a hydrogenation catalyst for 2 hours. When mass-spectrum measurement of reaction mixture was performed, the peak of  $C_{60}H_{18}$  considered to be a hydrogenation compound of a peak and  $C_{60}$  considered to be  $C_{70}H_{10}$ - $C_{70}H_{42}$  whose output is a hydrogenation compound of  $C_{70}$  -  $C_{80}H_{42}$  was measured. The ingredient to which the ingredient to which the presentation of this compound originates in  $C_{70}$  is 25%, and originates in  $C_{80}$  was 75%. The yield of these hydrogenation compounds was 121 mg. Next, the mixture of this hydrogenation compound was dissolved in 100 ml of toluene, DDQ(2,3-dichloro-5,6-dicyanobenzoquinone)3.0g was added as a dehydration agent, and it was made to react under 3-hour flowing back. When reaction mixture was separated by the neutral alumina column,  $C_{60}$ 84 mg and  $C_{70}$ 25 mg were obtained.

[0048]Example 2  $C_{70}$ (98% of purity, impurity toluene 2%)200mg is dissolved in 500 ml of toluene, 5.0g added and a 5% ruthenium / carbon (50%wet) was made to react at 120 kg of hydrogen pressure/cm<sup>2</sup>G, and the temperature of 180 \*\* as a hydrogenation catalyst for 6 hours. When mass-spectrum measurement of reaction mixture was performed, the peak of  $C_{60}H_{38}$  considered to be a hydrogenation compound of a peak and  $C_{60}$  considered to be  $C_{70}H_{10}$ - $C_{70}H_{38}$  whose output is a hydrogenation compound of  $C_{70}$  -  $C_{60}H_{62}$  was measured. The ingredient to which the ingredient to which the presentation of this compound originates in  $C_{70}$  is little, and originates in  $C_{60}$  was 100%. The yield of these

hydrogenation compounds was 115 mg. Next, the mixture of this hydrogenation compound was dissolved in 100 ml of toluene, DDQ(2,3-dichloro-5,6-dicyanobenzoquinone)3.0g was added as a dehydration agent, and it was made to react under 3-hour flowing back. When reaction mixture was separated by the neutral alumina column, C<sub>60</sub>105 mg was obtained, and a little C<sub>70</sub> were [ only being observed and ].

[0049]Comparative example 1C<sub>70</sub>(98% of purity, impurity toluene 2%)200mg is dissolved in 500 ml of toluene, 5.0g added and a 5% ruthenium / carbon (50%wet) was made for the temperature of 180 \*\* to react in hydrogen pressure 20 kg/cm<sup>2</sup>G as a hydrogenation catalyst for 2 hours. When mass-spectrum measurement of reaction mixture was performed, the peak of C<sub>60</sub>H<sub>32</sub> considered to be a hydrogenation compound of a peak and C<sub>60</sub> considered to be C<sub>70</sub>H<sub>30</sub>-C<sub>70</sub>H<sub>40</sub> whose output is a hydrogenation compound of C<sub>70</sub> - C<sub>60</sub>H<sub>44</sub> was measured. The ingredient to which the ingredient to which the presentation of this compound originates in C<sub>70</sub> is 60%, and originates in C<sub>60</sub> was 40%. The yield of these hydrogenation compounds was 125 mg. Next, the mixture of this hydrogenation compound was dissolved in 100 ml of toluene, DDQ(2,3-dichloro-5,6-dicyanobenzoquinone)3.0g was added as a dehydration agent, and it was made to react under 3-hour flowing back. When reaction mixture was separated by the neutral alumina column, C<sub>60</sub>42 mg and C<sub>70</sub>64 mg were obtained.

[0050]In this case, since the above-mentioned hydrogenation reaction is performed with the low hydrogen content pressure 20kg/cm<sup>2</sup>, that selectivity of what can obtain C<sub>60</sub> from C<sub>70</sub> is low, and insufficient as a method for obtaining C<sub>60</sub> from C<sub>70</sub>.

[0051]

[Effect of the Invention]According to this invention, the method of converting efficiently the fullerene of the with a carbon numbers [ , such as fullerene C<sub>70</sub>, ] of 70 or more amount of polymers with selectivity sufficient to fullerene C<sub>60</sub> can be provided. Namely, compared with fullerene C<sub>60</sub>, fullerene C<sub>60</sub> whose importance it is more useful and is high can be efficiently manufactured by the method of this this invention from the fullerene (C<sub>70+</sub>) of the with a carbon numbers [ with little / industrially / importance ] of 70 or more amount of polymers, It can contribute to improvement in the productivity of fullerene C<sub>60</sub> or its derivative remarkably.

[Industrial Application]When this invention is said in more detail about the alternative converting method to C<sub>60</sub> of the amount fullerene of polymers, it relates to the method of converting the fullerene of the with a carbon numbers of 70 or more amount of polymers into more useful fullerene C<sub>60</sub> with sufficient selectivity.

[0002]Fullerene C<sub>60</sub> is expected from various uses including the derivative.

For example, it is useful as those synthetic powder as exotic materials in various kinds of fields, such as electrical and electric equipment, electronic industry materials, etc., such as an electrical conducting material and a raw material of a super-conductor, and new materials.

[Description of the Prior Art]These days, the molecule-like carbon substance new type called the carbon cluster (spherical giant molecule) of the closed shell structural form of the carbon numbers 60 and 70 and 84 grades is compounded, and attracts attention. The carbon cluster which has this special structure is also called fullerene, is called fullerene  $C_{60}$ , the  $C_{70}$ , the  $C_{84}$ , etc. by the carbon number which constitutes that molecular skeleton, or is only called  $C_{60}$ ,  $C_{70}$ ,  $C_{84}$ , etc. Such fullerene is new carbon materials.

Since it is expected that unique physical properties will be shown also from having special molecular structure, research on the character and application development is advanced briskly.

[0004]It is the most fundamental fullerene with sufficient symmetry by the football type real ball-like unsaturation molecule from which  $C_{60}$  is constituted by six membered-rings and the five-membered ring also in the fullerene of the carbon number of these various kinds.

It is comparatively stable, and since it is easy to manufacture, attention is attracted especially in various kinds of areas of investigation and applicable fields, and expectation is the greatest also in respect of the use as a material with versatility new including the derivative.

[0005]thus, fullerene  $C_{60}$  forms the fields for 1 Otoshi including the derivative, and is especially useful as a raw material of a superconductor, etc. -- etc. -- the usefulness is becoming clear.

In various kinds of fields of the invention including the electrical and electric equipment and the electronic field, the expectation as an exotic material and new materials is becoming actual.

[0006]However, the fullerene of the with a carbon numbers [ , such as  $C_{70}$ , ] of 70 or more amount of polymers isolates, and although it is the stage currently studied, it is becoming clear that character, such as superconductivity which is looked at by fullerene  $C_{60}$ , is not shown.

[0007]That is, as industrial importance of these fullerene, the  $C_{60}$  is much larger than

other fullerene, such as  $C_{70}$ , and establishment of the art for obtaining fullerene  $C_{60}$  with more sufficient selectivity is desired strongly.

[0008]By the way, such fullerene is compounded by evaporating graphite by arc discharge (resistance heating method), or making it evaporate by a laser beam generally. In any case, it is obtained as soot containing the mixture of the fullerene of various kinds of carbon numbers.

There is little fullerene contained in this soot as about at most 10 % of the weight in all, among those fullerene, about 80 to 90% is fullerene  $C_{60}$ , and about 10 to 15% is  $C_{70}$ , and the other amount fullerene of polymers is also usually contained at a rate of several percent. Thus, although there is most fullerene  $C_{60}$  in the fullerene obtained, the byproduction of the fullerene ( $C_{70+}$ ) of the amount of polymers more than  $C_{70}$  is carried out at a remarkable rate. Separate recovery of the fullerene obtained as a mixture in soot is carried out by solvent extraction, chromatography separation, etc. as presentation fullerene, refining fullerene, isolation fullerene, etc.

[0009]Here, for the thing with large demand made the most important on industry and research to be fullerene  $C_{60}$  which shows superconductivity etc., and to raise the productive efficiency further, as described above is needed. On the other hand, from those, such as  $C_{70}$ , since the important position is not occupied so industrially, for the moment, the amount fullerene of polymers ( $C_{70+}$ ) seldom expects the remarkable increase in the demand, even if demand will see few especially also in the actual condition in the future. Therefore, unless the art of manufacturing fullerene  $C_{60}$  very selectively is developed, it is expected that the quantity of production of fullerene other than fullerene  $C_{60}$  becomes increasingly superfluous, so that the production quantity of fullerene increases.

[0010]Thus, in the production technology of the conventional fullerene, the badness of the balance of the quantity of production (comparatively) that shortage of fullerene  $C_{60}$  and the amount fullerene of polymers ( $C_{70+}$ ) are superfluous based on the remarkable difference in demand or usefulness had become a big problem.

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2.\*\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.